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Electrochromic artificial muscles based on nanoporous metal-polymer composites

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This work shows that a nano-coating of electrochromic polymer grown onto the ligaments of nanoporous gold causes reversible dimensional and color changes during electrochemical actuation. This combination of electromechanical and optical properties opens additional avenues for the applications of artificial muscles, i.e., a metallic muscle exhibits its progress during work by changing color that can be detected by optical means. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4827089]

Electrochemical actuators base on nanoporous metals with high surface-area-to-volume ratios, so-called metallic muscles,[1] represent a class of smart materials that undergo reversible dimensional changes upon changes in their interface electronic charge densities.[2–6] Here, we show that these metallic muscles become smarter when a thin electrochromic polymer coating is grown onto the ligaments of nanoporous metals: In addition, to the reversible dimensional changes taking place in the nanoporous metal during electrochemical actuation,[2–6] the polymer coating undergoes reversible changes in color upon electro-oxidation/reduction.[7,8] In this letter, we use nanoporous gold (NPG) as metallic muscle and polyaniline (PANI) as electrochromic conducting polymer to demonstrate the proof of principle.

A ∼60 mm-long metallic cantilever having a bilayer configuration was made.[5,9] The active part consists of a thick NPG layer with thickness ∼20 μm and the support is made of a relatively thin dense gold layer (∼7 μm). A schematic illustration of the bilayer strip cantilever is shown in Figure 1(a) and the typical bicontinuous nanoporous morphology of the active layer is displayed by the scanning electron micrograph of Figure 1(b). The average size of the ligaments and pores is ∼25 nm. A PANI coating with thickness between ∼5 and 10 nm was grown onto these ligaments by electrochemical oxidative polymerization of aniline from an aqueous solution containing 0.5 M of H_2SO_4 and 50 mM of aniline monomer.[10] The scanning and transmission electron micrographs of Figures 1(c) and 1(d), respectively, display a typical ∼5 nm thick uniform PANI coating grown onto the ligaments of NPG.

The first 10 cyclic voltammograms recorded during the growth of PANI onto the ligaments of NPG are shown in Figure 2. In the first cycle (red curve), the anodic deposition current increases at ∼1.1 V (versus Ag/AgCl reference electrode); this indicates that aniline initially oxidizes at a relatively high potential (∼1.1 V). A similar behavior has been reported during electrochemical deposition of aniline on diamond nanoparticles,[11] and on noble metals including bare platinum.[12] The oxidation of aniline at a relatively high voltage gives rise to degradation products, which are deposited onto the ligaments of NPG during subsequent cycles. This is illustrated by the two anodic peaks observed at ∼0.5 V and ∼0.7 V during the second and third cycles (blue curves).[11] The standard two pairs of redox peaks that characterize the oxidation (*oxi*) and reduction (*red*) of aniline at appropriate redox potentials, i.e., *oxi1*/*red1* at ∼0.3 V/0.1 V and *oxi2*/*red2* at ∼0.8 V/0.6 V only dominate from the fourth cycle (black curves). These two pairs of peaks are less pronounced compared to those reported during electrochemical deposition of aniline monomers onto bare noble metals electrode such as platinum.[12] In fact, the positions and amplitudes of these two pairs of redox peaks are well-known to be affected by the nature of the substrate onto which PANI is grown. The gradual increase in the current intensities of the voltammograms during subsequent cycles is commonly attributed to the auto-catalytic property of PANI for polymerization.

In the following, we present the simultaneous reversible changes in dimension and in color in our NPG/PANI hybrid material. We concentrate on a qualitative description of the material response; it is referred to Refs. 2–6 for quantitative

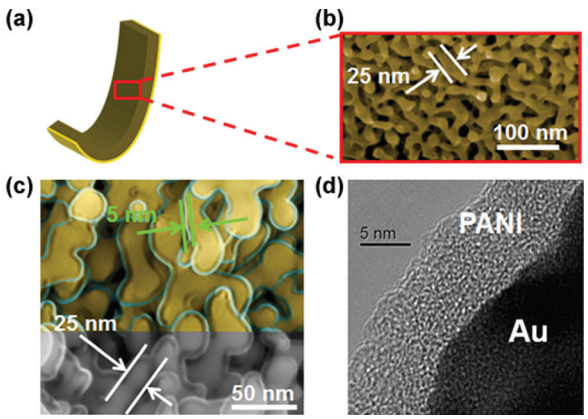

FIG. 1. Microstructural characterization. (a) The as-synthesized bilayer strip cantilever is initially bent because during dealloying the thick NPG layer shrinks,[6,13] whereas the thin dense gold layer does not. (b) Scanning electron micrograph showing the typical bicontinuous morphology of the thick NPG layer. (c, d) Scanning and transmission electron micrographs showing a typical ∼5 nm-thick PANI coating covering the ligaments of NPG.

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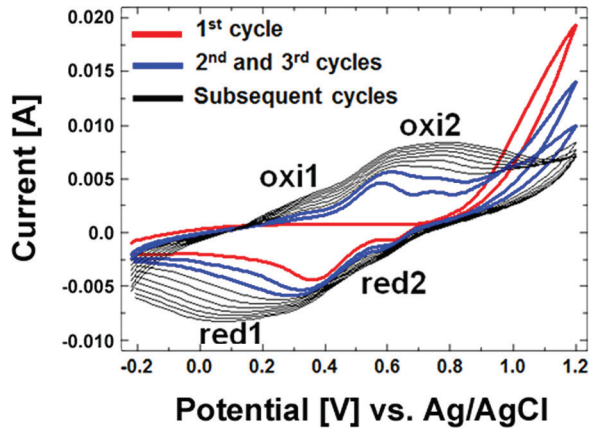

FIG. 2. Electrochemical polymerization curves. First 10 cyclic voltammograms recorded during the growth of PANI onto the ligaments of nanoporous gold.

studies on electrochemical actuation in nanoporous metals. After electrochemical polymerization, the NPG/PANI is actuated in the potential range between −0.22 V and 1.1 V (versus Ag/AgCl reference electrode), using as electrolyte a fresh aqueous solution containing 0.5 M of H_2SO_4 (without aniline). Note that the as-synthesized bilayer strip cantilever is initially bent as schematized in Figure 1(a). This is because during the dealloying process the thick nanoporous gold layer contracts, i.e., the well-known volume contraction during dealloying,[6,13] whereas the dense gold support does not. Typically, the as-synthesized green NPG/PANI cantilever expands during the forward scan and at the meantime it becomes dark blue. During reverse process the cantilever (initially dark blue) bends back to the initial shape and at the meantime it recovers its initial green color. This combination of electromechanical and optical properties broadens the potential of metallic muscles for many applications. A straightforward application might involve metallic muscles that can communicate while performing work, e.g., during work, the metallic muscle displays a certain color (in this case dark blue); when the work is done a different color is displayed (in this case green). Although electrochromic actuators can be made from pure polymer, the combination of a metal and a polymer for electrochromic actuation purposes is more attractive, because metallic actuators are stronger and stiffer than polymer actuators.[3]

The physical origin of the simultaneous changes in dimension and in color of the cantilever is the following: The NPG/PANI hybrid material takes advantage of the actuation ability of nanoporous metals on the one hand,[2–6] and the electrochromic properties of PANI on the other hand.[7,8] Starting with electrochemical actuation, Figure 3(a) displays the cyclic voltammograms recorded during the first 10 actuation cycles. These voltammograms display a pseudo-capacitive behavior associated with charge storage by the NPG/PANI composite.[10] Chen and co-workers have recently reported on a strong enhancement of the charge storage capacity of NPG/PANI hybrid materials in aqueous electrolyte.[10] This storage (release) of electronic charge by the NPG/PANI composite satisfies the requirement for reversible dimensional changes in conducting high surface-area-to-volume ratio nanostructured materials,[2–6] which explains the expansion and bending of our cantilever.

In addition to these reversible dimensional changes, the cantilever also undergoes reversible changes in color as schematized in Figure 3(b). As aforementioned, these changes in color are attributed to the electrochromic property of the PANI coating. Indeed, the color of PANI depends on its oxidation state and common colors include a dark blue color when PANI is fully oxidized (perningraniline), a green color when PANI is partially oxidized and doped (emeraldine salt), and a transparent color when PANI is not oxidized, which corresponds to the fully reduced form of PANI (leucoemeraldine).[7,8,14]

Before actuation, the NPG/PANI cantilever may display a green or a dark blue color depending on the doping state of PANI. In the present case, the as-synthesized NPG/PANI cantilever is green, i.e., at the end of the electropolymerization procedure, the PANI coating is partially oxidized and doped with H_2SO_4 (emeraldine salt).[7,8,14] Due to the electrochromic property of the PANI coating, the starting green color of our cantilever is susceptible to change to dark blue if PANI is further oxidized from its partial oxidation level to its full oxidation state. It is evident from Figure 3(a) that the two pairs of redox peaks *oxi1*/*red1* and *oxi2*/*red2* observed during electrochemical polymerization from Figure 2 are still present during electrochemical actuation, which indicates that PANI is being oxidized and reduced during actuation. These two redox activities in the PANI coating are responsible for the reversible changes in color observed in the cantilever during actuation: (A) During the forward anodic scan where the cantilever expands, green and dark blue colorations are observed (see illustration in Figure 3(b)). These two colors are justified by the following: (i) when the cantilever starts expanding, its initial green color is preserved at the first oxidation peak (i.e., *oxi1* in Figure 3(a)). This is because that peak corresponds to the oxidation of residual transparent leucoemeraldine (fully reduced form of PANI) to the green

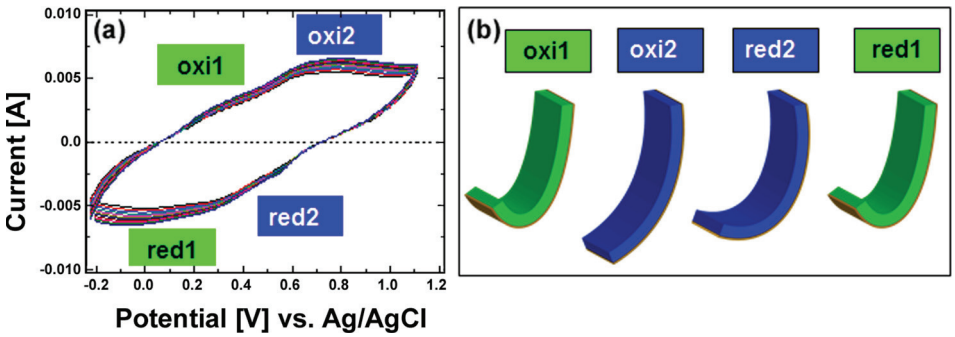

FIG. 3. Simultaneous reversible changes in dimension and in color: (a) Cyclic voltammograms recorded during the first 10 actuation cycles. (b) Simultaneous changes in color and in dimension in the bilayer cantilever.

emeraldine (partially oxidized form).[15,16] (ii) When the cantilever continues to expand, its color changes from green to dark blue. This is because at the second oxidation peak (i.e., *oxi2* in Figure 3(a)), the green emeraldine (partially oxidized form of PANI) is further oxidized to dark blue perningraniline (fully oxidized form of PANI).[15,16] (B) During the reverse cathodic scan where the cantilever bends back to its initial shape, dark blue, and green colorations are observed (see illustration in Figure 3(b)). These two colors are justified as follows: (i) when the cantilever starts bending back to its initial shape, the starting dark blue color is preserved despite the reduction activity present at the beginning of the reverse sweep as illustrated by the second reduction peak (i.e., *red2* in Figure 3(a)). This dark blue color is still present because the peak *red2* corresponds to the reduction of residual green emeraldine (partially oxidized form of PANI) to the transparent leucoemeraldine (fully reduced form of PANI).[15,16] Since the residual leucoemeraldine is colorless, the dark blue color of perningraniline (fully oxidized form of PANI) is still displayed. (ii) As the cantilever continues to bend back, its color changes from dark blue to green. This is because at the first reduction peak (i.e., *red1* in Figure 3(a)), the dark blue perningraniline (fully oxidized form of PANI) is partially reduced to the green emeraldine (partially oxidized form of PANI).[15,16] The redox activities at *oxi1*/*red1* and *oxi2*/*red2* clearly justify the reversible changes in color observed during the relaxation and bending of the cantilever. These two phenomena (reversible dimensional and color changes) are well-reproducible over many cycles because of the high stability of PANI.

In summary, we have demonstrated that a thin polymer coating can be exploited to add an additional functionality to nanoporous metals electrochemical actuators. By doing so, a metallic muscle becomes smarter because in addition to its reversible dimensional changes, it also undergoes reversible changes in color. This combination of electromechanical and optical properties opens other avenues for the applications of artificial muscles, i.e., a metallic muscle exhibits its progress during work by changing color that can be detected by optical means.

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